VOLUME 33 OCTOBER 1955 NUMBER 10

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EXAMPLES:

Atkins, K. R. 1954. Can. J. Phys. **32**: 347.
Dirac, P. A. M. 1947. The principles of quantum mechanics. 3rd ed. Oxford at the Clarendon Press.
——— 1948*a*. Phil. Mag. **39**: 31.
——— 1948*b*. Phys. Rev. **74**: 817.
——— 1952. Proc. Roy. Soc. (London), A, **212**: 330.
Smith, A. B. Unpublished.
Smith, A. B. and Allen, R. O. 1956. Can. J. Phys. In press.
Sumner, J. B. and Somers, G. F. 1944. Laboratory experiments in biological chemistry. Academic Press, Inc., New York, N.Y.

In the Text

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VOLUME 33 OCTOBER 1955 NUMBER 10

ON DIURNAL VARIATION IN COSMIC-RAY INTENSITY AT OTTAWA[1]

BY S. D. CHATTERJEE[2] AND J. N. BLOOM[3]

ABSTRACT

Cosmic-ray data from a high pressure integrating ionization chamber, obtained at Ottawa, for 129 complete days during September 1950 to July 1951 are subjected to rigorous statistical analysis. The barometric coefficient is -0.19% per mm. of Hg for the period covered by this analysis. The results also indicate a physically significant 24-hr. wave in cosmic-ray intensity, with an amplitude of 0.12% of the total intensity, having its maximum at about 10.40 a.m. local mean time. The existence of the semidiurnal wave, however, is not physically significant.

INTRODUCTION

The present work was undertaken to supplement the continuous measurements with counter telescopes by Rose (18) of the meteorological variations in cosmic-ray intensity at Ottawa. A phenomenological study of the influence of meteorological factors on the intensity–time variation of the different components of the cosmic radiation is of great value in localizing the origin of such perturbations. It has been established that these observed variations of intensity depend upon both the location of the observer and the physical phenomena producing them. For this reason, they are extensively studied at various stations spread wide over the globe.

A precise definition of the intensity of cosmic rays will naturally involve statements concerning the nature and range of energies of the rays, their directional properties and energy flux. All the necessary measurements for this purpose will require an elaborate series of experiments. However, a less detailed conception of the intensity of cosmic radiation may be adequate for many purposes. Accordingly it may be expressed as the rate of ionization in a gas confined in a vessel of known volume under certain conditions of 'shielding', and exposed to cosmic radiation from all directions. In practice, however, no standard has been adopted by investigators either in the type of vessel or regarding the extent of shielding. Furthermore, most of them have not based their conclusions on modern statistical reasoning. The importance of rigorous statistical analysis of such data was first shown by Forbush (8). It is essential

[1]*Manuscript received May 1, 1955.*
Contribution from the University College of Science, Calcutta, India. (The measurements were taken at the Division of Physics, National Research Council, Ottawa, Canada.)
[2]*Now at the University College of Science, Calcutta, India.*
[3]*Now at Defence Research Telecommunications Establishment, Ottawa, Ontario.*

that the raw data be corrected for known correlations, before being subjected to harmonic analysis for unknown periodic relationships.

The present paper, first in a series, deals exclusively with the so-called barometer effect and diurnal variation analysis. It is proposed to take up the magnetic storm effects and cosmic-ray bursts in subsequent communications.

APPARATUS

The ionization chamber consists of a steel cylinder, with a net volume of 20.4 liters, filled with pure argon at 40 atmospheres pressure. The ionization current in the main chamber due to incident cosmic rays is balanced by the current in an auxiliary chamber produced by α-particles from an adjustable surface of metallic uranium. As suggested by Swann (20), the potentials applied to the two chambers are distributed by means of a potentiometer in such a way that the resistances in the two limbs of the potentiometer are inversely proportional to the coefficients of induction of the main and auxiliary chambers to the electrode system. Under these conditions a change in the voltage of the battery will leave the electrode potential unaltered.

The difference between the two ionization currents is measured with a Lindemann electrometer, housed in an air-tight and dried chamber. The shadow of the electrometer needle is projected through a microscope onto a continuously moving strip of 3 in. Kodak bromide paper. The photographic paper is moved by a synchronous motor with a reduction gear such that the paper speed is about three inches per hour. Besides the departure from balance of the cosmic-ray ionization, the barometric pressure and temperature are also roughly indicated on the same strip of paper.

Fig. 1 shows a typical record. The wavy white line is the trace of the electrometer needle for a period of about 55 min., during which period the collecting electrode is insulated. The next successive sequence of events, occupying an interval of about five minutes, consists in the following operations:

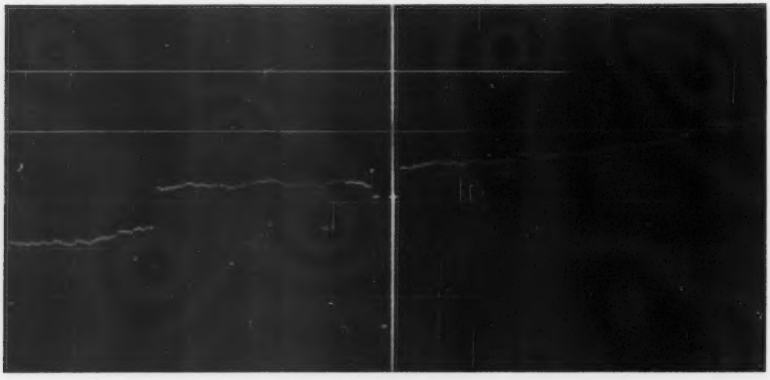

FIG. 1.

(*a*) earthing the collecting electrode,

(*b*) applying a calibration voltage of 0.5 volts to it,

(*c*) earthing it again,

(*d*) breaking the lamp-circuit,

(*e*) restoring the illumination, and

(*f*) insulating the collecting electrode.

All these operations are performed automatically by microswitches and relays, the timings being carefully adjusted by suitable cams mounted on a common axis and rotated by a synchronous clock motor at the rate of one revolution per hour.

Further details about the ionization chamber and its associated equipment will appear elsewhere. The working principle is similar to that of the C-1 meter designed by Compton, Wollan, and Bennet (3) and the sensitivity is nearly the same.

REDUCTION OF OBSERVATIONS

The ionization chamber was surrounded on all sides by lead bricks of 10 cm. thickness and located in an unused rifle range with concrete walls and roof of about two feet thickness. The total ionization produced within the chamber by cosmic rays alone was found to be 72 ions/cc./sec. Measurements were begun on September 7, 1950, and continued during the months of October and November. Then, there was a break during the months of December 1950 and January 1951, when the range was pulled down. The ionization chamber was reinstalled in a new building forming the cosmic-ray wing of the Montreal Road laboratory in January and the measurements were continued until July 1951. Not all daily observations were continuous, i.e. on some days there were less than 24 hourly observations, on account of power failure or faults developed in the instrument. These days we shall call incomplete days. While under ideal conditions these incomplete days can be combined with the complete days for the specific purpose of fluctuation analysis, practical limitations have prompted us to consider the complete days alone for the purpose of this part of the work.

These incomplete days will not be entirely ignored and we shall use them in the study of bursts and of geomagnetic effects. Thus, we have 40 complete days during Period I (September–November 1950), 34 during Period II (January–March 1951), and 55 during Period III (March–June 1951). The hourly ionization records were maintained according to G.M.T., but the barometric pressure in millibars was kept according to local time, which is normally five hours behind G.M.T. or four hours during daylight saving periods. Calculations were made with reference to local mean time only.

The first step in our reduction of data was to obtain the deflection for each hour at the standard calibration, viz. 30 divisions per volt, after deducting the deflections due to bursts, if any. Thus, we obtained

$$X_t = 30(N_t - n_t)/d_t, \qquad [1]$$

where N_t represents the hourly departure (during hour t) from balance of the cosmic-ray ionization in number of divisions of scale marked on the photographic paper;

n_t = deflection in number of divisions due to cosmic-ray bursts, which appeared as a sudden vertical displacement in the direction of increased ionization of the ionization track, during that hour t;

d_t = deflection in number of divisions due to a calibrating voltage of 1.0. At normal sensitivity, it was arranged to be 30 divisions per volt.

We also obtained

$$Y_t = (p_t - 1000), \tag{2}$$

where p_t is the barometric pressure in millibars (mb.) at the hour t.

These X_t's and Y_t's were then averaged for each day obtaining $\overline{X_t}$'s and $\overline{Y_t}$'s where $i = 1, 2, \ldots, 129$, and the bar indicates the average. These pairs of mean values for 129 complete days were then subjected to regression analysis and to harmonic analysis.

Usually, the variation in the intensity of cosmic rays due to the change in barometric pressure is recorded as ions/cc./sec./mm. or as per cent of total intensity/mm. In order to reduce the tedium the computations were made before conversion of the data to the final units. In the present equipment it was found that one division of deflection corresponds to 0.178 ion/cc./sec. Thus we obtained the barometric effect in terms of ion/cc./sec./mb. In order to express the barometric effect as ion/cc./sec./mm. of Hg we have the conversion factor

$$C = 0.178 \times 1013/760 = 0.237 \text{ ion/cc./sec./mm. of Hg.} \tag{3}$$

BAROMETER EFFECT

Before attempting to interpret these ionization records, it is necessary to allow for changes brought about by the variation of atmospheric pressure.

We assume, for the ranges of pressure encountered at the station, a linear relation between the observed daily mean of barometric pressure $\bar{Y}$ and the daily mean of departure from balance $\bar{X}$—of the form

$$\bar{X}_{1000} = \bar{X}_p - \beta(\bar{Y} - 1000), \tag{4}$$

where $\bar{X}_{1000}$ is the calculated value of $\bar{X}_p$ for $p = 1000$ mb.

The regression coefficient β multiplied by the conversion factor C gives B, the barometric coefficient. B has been calculated by the method of least squares for:

(i) the months of September, October, and November (1950) and February, March, April, and May (1951) individually,

(ii) periods I, II, and III, and

(iii) 129 complete days.

Table I gives these values together with their standard deviations. All these

TABLE I

REGRESSION-COEFFICIENT β, ITS STANDARD DEVIATION σ_β, "STUDENT'S" $t = \beta/\sigma_\beta$, BAROMETRIC COEFFICIENT (B) EXPRESSED AS CHANGE IN RATE OF IONIZATION IN ION/CC./SEC./MM., AND PERCENTAGE CHANGE IN IONIZATION PER MM. OF PRESSURE

Period	No. of days	β	σ_β	t	B	$100B/72$
I	40	−0.5818	0.1145	−5.08	−0.138	−0.191
II	34	−0.7144	0.1603	−4.46	−0.169	−0.234
III	55	−0.5529	0.1219	−4.54	−0.131	−0.181
Sept. 1950	10	−0.7833	0.1542	−5.08	−0.186	−0.258
Oct. 1950	14	−0.8013	0.0658	−12.17	−0.190	−0.263
Nov. 1950	16	−0.4153	0.0959	− 4.33	−0.099	−0.137
Feb. 1951	19	−0.6973	0.0304	−22.92	−0.165	−0.229
March 1951	19	−0.5522	0.1063	− 5.21	−0.131	−0.182
April 1951	28	−0.5448	0.0764	− 7.13	−0.129	−0.179
May 1951	19	−0.8089	0.0520	−15.56	−0.192	−0.266
Total (129 days)	129	−0.5747	0.1190	− 4.83	−0.136	−0.188

values of B have been found to be significant showing that there is a real barometer effect on the variations in cosmic-ray intensity.

Furthermore, we have selected two sets A and B of eight days of increasing and decreasing pressure respectively and computed regression coefficients of bihourly averages for these two sets. Table II shows the computation.

TABLE II

Period	β	σ_β	t	Significance 1% level	B	$100B/72$
A, increasing pressure (hourly means)	−0.5362	0.0431	−12.44	Significant	−0.127	−0.176
B, decreasing pressure (hourly means)	−0.6074	0.0354	−17.16	Significant	−0.144	−0.200
A and B (hours 1–2)	−0.5711	0.0413	−13.83	Significant	−0.135	−0.187
A and B (hours 7–8)	−0.6086	0.0301	−20.22	Significant	−0.144	−0.200
A and B (hours 13–14)	−0.5192	0.0278	−18.68	Significant	−0.123	−0.170
A and B (hours 19–20)	−0.6738	0.0610	−10.46	Significant	−0.160	−0.208

Thus, it is found that there is no significant difference between these values and those obtained for daily means. We may therefore say that the barometric coefficient does not differ significantly for different hours of the day. Accordingly we may represent the percentage change in ionization per mm. of Hg as −0.19 at Ottawa.

THE ANALYSIS OF THE DIURNAL AND SEMIDIURNAL VARIATIONS

During the earlier stages of cosmic-ray investigations, great emphasis was laid upon the determination of the diurnal variation of intensity. It was thought that a knowledge of the diurnal variation would give a clue to the

origin of primary radiation, having established that the radiation was of extraterrestrial origin. The results quoted by Corlin (4) showed relatively large amplitudes with solar and sidereal periods. However, recent studies based on improved techniques have shown that the solar diurnal variation of cosmic-ray intensity is only about 0.2% in amplitude.

Our raw material for the analysis of daily variation consisted for each day of 12 bihourly means of departure from balance, exclusive of bursts. Each of these 12 values was first corrected for the corresponding bihourly means of pressure by means of the equation

$$\bar{X}_{1000} = \bar{X}_p - \beta(\bar{Y} - 1000).$$

These sets of 12 values of departure from balance were then subjected to harmonic analysis, providing two sets of harmonic coefficients (a_1, b_1) and (a_2, b_2) for each day. In determining these coefficients we followed the method due to Whittaker and Robinson (24). Following Bartels (2), we can draw a 24-hr. harmonic dial, on which each day is characterized by a point with Cartesian co-ordinates of its first harmonics a_1 and b_1. Similarly, a 12-hr. dial was constructed in which each point may be conceived as the end point of a clock hand which indicates the time of the wave maximum, and whose length indicates the amplitude of the wave. For 129 days, we have on each dial a cloud of 129 points and the analysis of the variability of these harmonics is connected with the analysis of the geometrical properties of these clouds.

We have refrained from applying noncyclic corrections to these harmonics as we are not quite sure that the noncyclic variation is due to a linear function. It may also be noted that there has been some discussion on the feasibility of such corrections by Bartels.

Figs. 2 and 3 show the harmonic dials for the 24-hr. and the 12-hr. wave for periods I, II, and III. The time-maximum of the 24-hr. wave is at 10.40 a.m., having an amplitude of 0.12%. The time-maximum of the 12-hr. wave appears to be at 11 a.m. with an amplitude of about 0.01%.

To test for the ellipticity of the distribution of the harmonic constants, we have followed Mauchly's (13) method, and none of the six distributions has been found to be elliptical. Probable error circles were then drawn using the formula

$$P_i = 0.833 M_i, \quad i = 1, 2, \tag{5}$$

where P_i is the probable radius and

$$M_i = (\sigma_{a_i}{}^2 + \sigma_{b_i}{}^2)^{\frac{1}{2}}, \quad i = 1, 2.$$

It may be seen that the number of points inside the circle is very nearly the same as that outside of it. Assuming for the moment that the points for successive days are independent, the radius of the probable error for the mean can be calculated by the formula

$$P_i(\text{mean}) = (1/\sqrt{n}) P_i(\text{individual points}), \tag{6}$$

where n is the number of points on the dial.

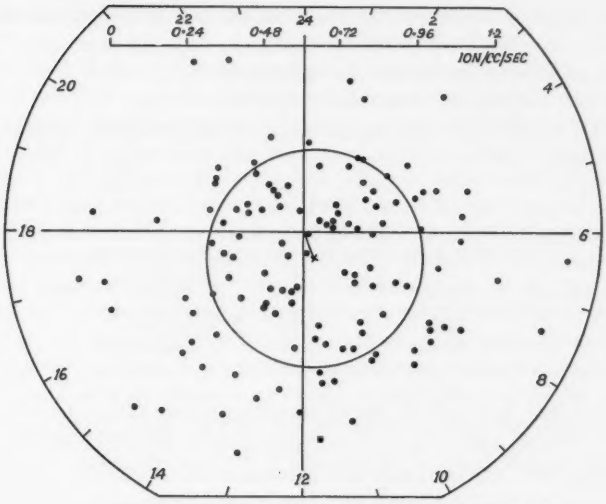

FIG. 2. 24-HOUR HARMONIC DIAL, APPARENT COSMIC-RAY INTENSITY FOR 129 COMPLETE DAYS.

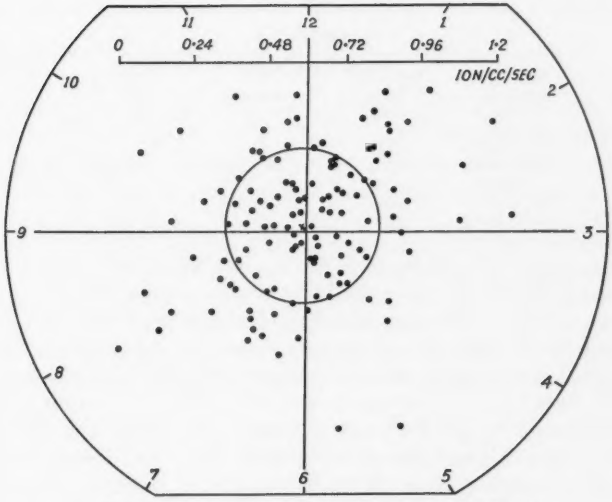

FIG. 3. 12-HOUR HARMONIC DIAL, APPARENT COSMIC-RAY INTENSITY FOR 129 COMPLETE DAYS.

We now proceed to discuss the reality of the average amplitude of each of the two clouds. For this purpose, we apply

(1) Schuster's test (see 11, for example), and

(2) the test criterion proposed by Hartley (9).

Tables III and IV show the application of these tests to the whole set of 129 complete days.

TABLE III

SCHUSTER'S TEST

Wave	K	Significance 1% level
24-hr.	8.52	Significant
12-hr.	3.65	Not significant

Schuster's test is based on the strict independence of points of successive days and random walk conditions. According to Schuster, the probability P_S that an empirical squared amplitude is K times the mean squared amplitude is:

[7] $$P_S = e^{-K}.$$

If this is very low, we may accept the observed wave as real. In this connection, it may be noted that Tintner (21) and Kendall (11, for example) have raised some objections against this and similar tests. On the other hand, Hartley claims that his test "meets most of Kendall's objections."

TABLE IV

HARTLEY'S TEST

Source	Sum of squares	Degrees of freedom, D.F.	Mean square	Fisher's "F"	Significance 1% level and 5% level
Total	5755.7460	1547			
24-hr. wave	118.4638	2	59.2318	16.22	Significant
12-hr. wave	4.6905	2	2.3453	$\simeq 1$	Not significant
Residual	5632.5920	1543	3.6504		

Thus, by using either Schuster's test or Hartley's test, we find that the 24-hr. wave is significant, while the 12-hr. wave is not significant.

However, some investigators including Forbush (8) have concluded that there exist both a physically significant 24-hr. wave and a physically significant 12-hr. wave. Unfortunately, with the solitary exception of Forbush, no other author has based his conclusion on modern statistical reasoning. Forbush himself has based his conclusion on Schuster's test only. The actual result of Hartley's test on Forbush's data is not known to us. It is rather difficult to make a comparative study of the measurements of the D-effect made by different authors. First, the apparatus measuring the intensity is either a G-M counter or an ionization chamber. They are usually different in size and

sometimes in contents also. Secondly, the angle of cone ϕ formed by the observed radiation is in many cases wide and in others narrow. In some experiments as that of Rau (16) only energetic mesons, having initial energy greater than 10^{10} ev., could penetrate into the ionization chamber in a narrow vertical angle; whereas, in some other counter experiments like Duperier's (6) not only was the angle ϕ very wide but also there were no absorbers. Furthermore, some have not applied a barometric correction, while others have made an 'external air temperature' correction. Facing such diverse types of observation and variety of reduction procedure, we hesitate to make an over-all comparison. However, the D-effect has been generally verified by many investigators, including Hess and Graziadei (10), Forbush (8), Duperier (6), and Doan (5), although the phase relationship between their results is rather uncertain.

According to Wait (Ref. 8, p. 16, for example) the gamma-ray content of the atmosphere appears to fluctuate with an amplitude as much as 0.3 ion/cc./sec. with a maximum about noon. It is possible that ionization records are affected by these fluctuations. However, the wide phase variation of the D-effect is very unlikely to be explained by these fluctuations.

Vallarta and Godart (23) suggested that the variation in character of the experimentally observed D-effect could be accounted for at high latitudes by a heliomagnetic field and at low latitudes by fluctuations in the geomagnetic field. Malmfors (12) showed that such explanations were incompatible with the results found by Alfvén and Malmfors (1). Recently, however, Trumpy (22) has reported changes in cosmic-ray intensity during magnetic storms which show a distinct diurnal variation. This aspect of the variation will be considered in the next part of our work.

Thus, the physical explanation of the effect has not been satisfactorily given so far.

S VARIATION

Some investigators, like Regener and Rau (17), Ehmert (7), Rau (16), and Sarabhai (19), have found a daily variation in meson intensity which is mainly semidiurnal and shows a strong positive correlation with that in atmospheric pressure. Several authors have suggested that this phenomenon is explicable in terms of Pekeris' (15) theory of atmospheric oscillations. This aspect of the problem has been studied in detail by Nicolson and Sarabhai (14) who use the symbols +S and −S to imply that the time-maximum of the intensity variation is displaced by less than one hour from the time-maximum or time-minimum of the semidiurnal pressure variation. The experimental data suggest that although the intensity measured under a thick absorber shows a +S variation, that measured without an absorber shows a −S variation.

In our present investigation, let us suppose (ignoring the results of Hartley's test on the 12-hr. dial) that there is a real semidiurnal variation in meson intensity. We next find the angle between the vectors representing the mean of the intensity cloud and the mean of the pressure cloud. If this is less than $\pm 30°$, we get a +S variation, whereas if it lies between 150° and 210° we get a

$-$S variation. Table V shows that the angle between the vectors is 78°17′. So, we get neither $+$S nor $-$S variation.

TABLE V

SEMIDIURNAL VARIATION
(for 129 days)

Mean of	a_2	b_2	a_2/b_2	$\tan^{-1}(a_2/b_2)$
Intensity cloud m_i	$+0.0622$	-0.0468	-1.329	126°55′
Pressure cloud m_p	-0.1068	-0.2272	0.470	205°12′

Angle between these mean vectors =78°17′.

In the case of the S variation, the only results of convincing statistical significance are those of Duperier and Rau. Duperier obtained a $-$S variation having the value $-(0.18,\ 03^h\ 12^m)$, while Rau got a $+$S of the magnitude $+(0.18,\ 11^h\ 30^m)$. On account of more well-defined experimental conditions and freedom from magnetic fluctuations, Rau's results have been considered less ambiguous for the purpose of interpretation. It must be pointed out, however, that Rau's values have been obtained without correction for pressure. Moreover, the objections of Nicolson and Sarabhai against barometric correction do not appear to be convincing. It has been almost firmly established that a great part of the intensity variation can be explained by the barometer effect. Before picking out the cycles, if any, in a time-series, it is only proper to eliminate the trend and it could be wrong to subject the uncorrected data themselves to harmonic analysis. It would be interesting to check Rau's data for $+$S variation after correcting for pressure.

DISCUSSION OF RESULTS

Unfortunately, owing to want of some more information, our own results are not very satisfactory. Cosmic rays travelling through the atmosphere gradually lose energy in different ways and the amount of loss depends on the air-mass traversed. On account of the instability of the meson, the penetrating rays are also subject to the process of decay. A proper view of the cosmic-ray intensity should therefore be that at sea-level; it is a function of the mass of air and of the change in height of the pressure-level at which mesons are generated. These may be called the "mass absorption effect" and the "decay effect." It is not yet decisively known where mesons are produced, assuming that they are produced within a single layer.

Following Duperier (6) the regression equation may be expressed as

$$[8] \qquad C-C_m = \mu(B-B_m)+\mu'(H-H_m),$$

where C, B, and H are the intensity of cosmic rays, barograph reading, and height respectively and the subscript 'm' refers to mean values. On this basis, μ represents the true absorption coefficient in air and μ' the mean rate of decay of mesons. It is clear that β, the regression coefficient of equation [4], will in general be greater than μ. No upper air sheets are available for the Ottawa

station for the period 1950–51. Efforts are however being made to obtain these data for nearby stations in order to find out the possibility of interpolation. Until then, we shall have to depend on the present values which have been partly eliminated for trend.

In conclusion, it may be said that our data show that

(1) there is a real 'barometer effect',

(2) there is a physically real diurnal wave but not a real semidiurnal wave in cosmic-ray intensity, and

(3) there is no $+S$ or $-S$ variation.

ACKNOWLEDGMENTS

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THE RAMAN SPECTRUM OF ETHANE[1]

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ABSTRACT

The rotational and rotation-vibrational Raman spectra of gaseous ethane at 1–3 atm. pressure have been photographed with a spectral resolution of approximately 1 cm.$^{-1}$. Analyses of the rotational structures of the ν_1 and ν_2 totally symmetric bands were carried out; only the Q branch of the ν_2 band was observed. The structures of the degenerate ν_{10} and ν_{11} bands were analyzed; however, no trace of ν_{12} was found. The structure of the ν_{10} band shows beyond doubt that the point group of the molecule is $\mathbf{D}_{3d}$. From the $\nu_{11}+\nu_4$ infrared band, and the ν_{11} Raman band, the value, 278.4 cm.$^{-1}$, is deduced for the torsional frequency ν_4.

INTRODUCTION

Although a large amount of information on the infrared spectrum, the Raman spectrum, and the heat capacity of ethane has been accumulated, there are still uncertainties regarding the structure and the constants of the molecule. Measurements of the specific heat at low temperatures (8, 9, 15) have shown that there is no free rotation of the two methyl groups relative to one another about the C—C axis; however, the equilibrium configuration is not known with certainty. Also, no accurate spectroscopic evaluation of the torsional frequency has yet been made. In the present investigation the newly developed techniques for Raman spectroscopy of gases have been used in an attempt to elucidate these and other problems concerning the ethane molecule.

There are two plausible configurations for the molecule in the equilibrium position: the eclipsed model (point group $\mathbf{D}_{3h}$) in which there is a plane of symmetry perpendicular to the threefold C—C axis, and the staggered model (point group $\mathbf{D}_{3d}$) with a center of symmetry. Table I, adapted from Herzberg (6), gives the designation, description, species, and activity of the 12 fundamentals for both models. For the $\mathbf{D}_{3d}$ configuration the rule of mutual exclusion holds: transitions active in Raman scattering are not active in infrared absorption, and vice versa. For the $\mathbf{D}_{3h}$ model, on the other hand, the doubly degenerate vibrations ν_7, ν_8, and ν_9 exhibit both Raman and infrared activity. It would thus seem that the two point groups could be easily distinguished. However, if the three infrared active bands ν_7, ν_8, and ν_9 are not observed in the Raman effect, they may be only very weak and not necessarily forbidden in the sense of the symmetry selection rules. Table I shows that a better method of determining the point group is available when the rotational structure of the Raman bands of the gas is sufficiently well resolved: for the E_g bands of the $\mathbf{D}_{3d}$ model there are two series of Q branches ($\Delta K = \pm 1, \pm 2$), whereas for each of the degenerate types, E' and E'', of the $\mathbf{D}_{3h}$ model there is only one

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TABLE I

THE NORMAL VIBRATIONS OF THE TWO MODELS FOR C_2H_6

Designation	Description	D_{3h} (eclipsed model)		D_{3d} (staggered model)	
		Species	Activity*	Species	Activity*
ν_1	CH stretching	A_1'	R. $\Delta K = 0$	A_{1g}	R. $\Delta K = 0$
ν_2	CH_3 deformation	A_1'	R. $\Delta K = 0$	A_{1g}	R. $\Delta K = 0$
ν_3	C—C stretching	A_1'	R. $\Delta K = 0$	A_{1g}	R. $\Delta K = 0$
ν_4	Torsion	A_1''	Inactive	A_{1u}	Inactive
ν_5	CH stretching	A_2''	I. $\parallel$	A_{2u}	I. $\parallel$
ν_6	CH_3 deformation	A_2''	I. $\parallel$	A_{2u}	I. $\parallel$
ν_7	CH stretching	E'	I. $\perp$, R. $\Delta K = \pm 2$	E_u	I. $\perp$
ν_8	CH_3 deformation	E'	I. $\perp$, R. $\Delta K = \pm 2$	E_u	I. $\perp$
ν_9	Bending	E'	I. $\perp$, R. $\Delta K = \pm 2$	E_u	I. $\perp$
ν_{10}	CH stretching	E''	R. $\Delta K = \pm 1$	E_g	R. $\Delta K = \pm 1, \pm 2$
ν_{11}	CH_3 deformation	E''	R. $\Delta K = \pm 1$	E_g	R. $\Delta K = \pm 1, \pm 2$
ν_{12}	Bending	E''	R. $\Delta K = \pm 1$	E_g	R. $\Delta K = \pm 1, \pm 2$

**R. and I. denote activity in Raman scattering and infrared absorption respectively. For the Raman active vibrations the selection rules for the quantum number, K, are given; this information is more relevant for resolved bands than the state of polarization.*

series. The torsional oscillation, ν_4, is inactive as a fundamental in both infrared absorption and Raman scattering; however, its first overtone is Raman active and various combination tones involving ν_4 are Raman or infrared active.

The Raman spectrum of gaseous ethane has been studied by Bhagavantam (1) and Lewis and Houston (10). In addition to the Q branches of several totally symmetric bands, the latter authors observed some structure in the 2900–3000 cm.$^{-1}$ region which is apparently a part of the degenerate ν_{10} band. This structure was further resolved in an unpublished investigation by Griffiths (5) in this laboratory, and identified beyond a doubt as a series of Q branches of the ν_{10} band. In addition, a broad unresolved band of medium intensity with a maximum at 1478 cm.$^{-1}$ was observed and assigned to the degenerate ν_{11} vibration. This band may correspond to the depolarized line at 1460 cm.$^{-1}$ reported in liquid ethane (2, 4), and also to the weak band at 1460 cm.$^{-1}$ observed in the gas by Bhagavantam.

The exhaustive study by Smith (13) is the most recent of many investigations of the infrared spectrum of ethane. A comprehensive discussion of the infrared and Raman data has been given by Herzberg (6).

EXPERIMENTAL

The equipment used in this investigation has been described elsewhere (14). The reciprocal linear dispersion of the spectrograph at 4358 Å is 10.5 cm.$^{-1}$ per mm. Ethane gas* of high purity was used at pressures of 1 to 3 atm. Most of the spectrograms were recorded on Kodak 103a–0 spectroscopic plates using a spectral slit width of 0.7 cm.$^{-1}$. The spectra were measured as described in References (3) and (12). In determining the Raman shifts the values 22,938.04 and 24,705.30 cm.$^{-1}$ were used for the frequencies of the Hg4358 and Hg4047 lines, respectively.

**Obtained from Phillips Petroleum Company, Bartlesville, Okla., U.S.A.*

RESULTS AND DISCUSSION

As will be shown, this investigation indicates that the equilibrium configuration of the ethane molecule is $\mathbf{D}_{3d}$; thus, from Table I, there should be three totally symmetric and three doubly degenerate Raman active fundamentals. All three totally symmetric bands were observed; extensive rotational structures of ν_1 and ν_3 were measured, but only the Q branch of ν_2 could be recorded. The structures of the degenerate bands ν_{10} and ν_{11} were sufficiently resolved to permit a fairly complete analysis, but no indication of the ν_{12} band was found. In addition, the pure rotational Raman band was measured.

The Rotational Spectrum

The rotational spectrum excited by Hg4358 was photographed with a gas pressure of 2 atm. Without the cylindrical lens in front of the photographic plate (14) exposure times up to 40 hr. were required. The frequency shifts are given in Table II. The stray light present in these exposures prevented the measurement of lines with frequency shifts less than 33 cm.$^{-1}$.

TABLE II

ROTATIONAL RAMAN SHIFTS OF C_2H_6

$\Delta\nu$ (cm.$^{-1}$)	Assignment	$\Delta\nu$ (cm.$^{-1}$)	Assignment
33.15	$S(11)$	62.19	$S(22)$
35.82	$S(12)$	64.84	$S(23)$
38.41	$S(13)$	67.44	$S(24)$
40.98	$S(14)$	70.08	$S(25)$
43.64	$S(15)$	72.80	$S(26)$
46.30	$S(16)$	75.42	$S(27)$
48.98	$S(17)$	77.92	$S(28)$
51.72	$S(18)$	80.48	$S(29)$
54.27	$S(19)$	83.26	$S(30)$
56.91	$S(20)$	85.88	$S(31)$
59.56	$S(21)$	88.51	$S(32)$

The rotational selection rule for a symmetric top is $\Delta J = 0, +1, +2$, $\Delta K = 0$, where J is the total angular momentum and K its component along the figure axis. Both R and S branches should therefore be present in the spectrum. However, since the ratio of the moments of inertia, $I_A/I_B \backsim 0.25$, is small, the R branch is relatively weak (11) and was obscured in the spectrograms by the stray light in the neighborhood of the exciting line. The Raman shifts for the S lines ($\Delta J = +2$) follow the relation

$$|\Delta\nu| = B_0(4J+6) - D_J(4J+6)(2J^2+6J+6) - D_{JK}(4J+6)K^2, \quad J, K = 0, 1, 2, \ldots,$$

where $B_0 = h/8\pi^2 cI_B^0$ and $D_J \ll B_0$. The term in D_{JK} may be neglected. The plot of $|\Delta\nu|$ against J is nearly a straight line, and the ratio of the slope to the intercept, which is 2/3, can be used to establish the correct J numbering of the lines. The values of the constants B_0 and D_J are obtained by plotting $|\Delta\nu|/(4J+6)$ against $2J^2+6J+6$. A least squares analysis of the 22 observed frequencies in Table II gave the values $B_0 = 0.6627 \pm 0.0004$ and $D_J = 10.6 \times 10^{-7}$ cm.$^{-1}$. These are in satisfactory agreement with the values given by Smith,

$B_0 = 0.66259 \pm 0.00013$, determined from the structure of parallel infrared bands, and $D_J = 6.00 \times 10^{-7}$ cm.$^{-1}$, calculated from the theoretical formula of Howard (7). The latter values are undoubtedly somewhat more accurate and will be used in the following analyses.

The 900–1100 cm.$^{-1}$ Region

Lightly exposed spectrograms in the 900–1100 cm.$^{-1}$ region of Raman shifts excited by Hg4358 showed a strong line with intensity degraded towards lower frequency shifts and with a maximum at 994.2 cm.$^{-1}$; this line, measured by Bhagavantam (1) and Lewis and Houston (10) at 993 cm.$^{-1}$, is the Q branch of ν_3, the totally symmetric C—C stretching vibration. With a gas pressure of

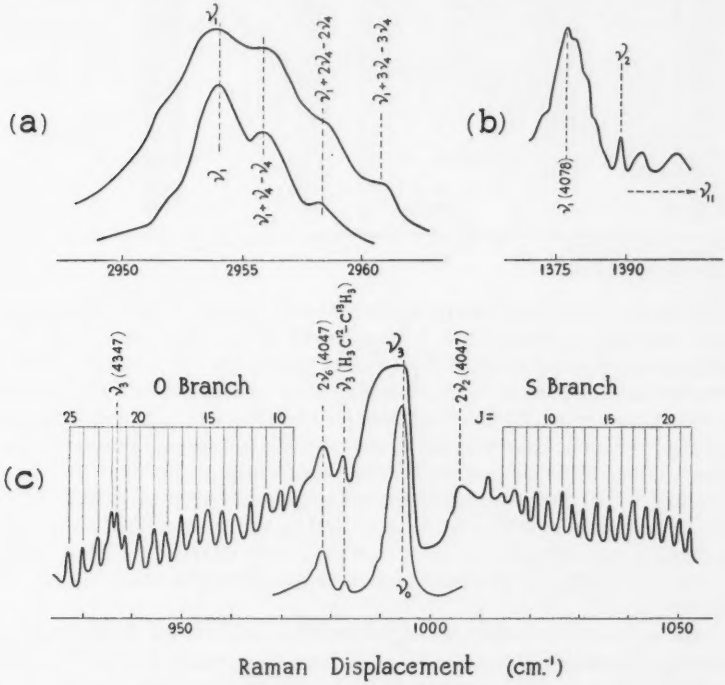

FIG. 1. Microphotometer traces of the totally symmetric bands of ethane. (*a*) Lightly exposed spectrograms of ν_1 showing the structure of the Q branch. (*b*) The Q branch of the weak ν_2 band. (*c*) A heavily exposed spectrogram of the ν_3 band with $NaNO_2$ filter and a lightly exposed spectrogram without the filter.

3 atm. and an exposure time of 48 hr. using a sodium nitrite filter, many more lines were recorded as shown in Fig. 1(*c*). Most of the fainter lines were identified as belonging to the O and S branches of the ν_3 band (Table III). Since the selection rule for totally symmetric vibrations is $\Delta J = 0, \pm 1, \pm 2$, P and R branches should also be observed. However, just as for the rotational spectrum,

TABLE III

RAMAN FREQUENCIES OF C_2H_6 IN THE 900–1100 CM.$^{-1}$ REGION

$\Delta\nu$ (cm.$^{-1}$)	Assignment		$\Delta\nu$ (cm.$^{-1}$)	Assignment	
	ν_3 Band	Other features		ν_3 Band	Other features
920.9	$O(27)$		982.1	$\nu_3(H_3C^{12}—C^{13}H_3)(Q_{max})$	
926.9	$O(25)$		994.2	$\nu_3(Q_{max})$	
929.7	$O(24)$		2779.8†		$2\nu_2(Q_{max})$
932.7	$O(23)$		2784.4†		$-(Q_{max})$
935.7	$O(22)$		1016.8	$S(7)$	
994.1*		$\nu_3(Q_{max})$	1019.2	$S(8)$	
938.3	$O(21)$		1021.4	$S(9)$	
941.1	$O(20)$		1023.7	$S(10)$	
944.2	$O(19)$		1026.3	$S(11)$	
946.9	$O(18)$		1028.7	$S(12)$	
949.6	$O(17)$		1031.1	$S(13)$	
952.6	$O(16)$		1033.6	$S(14)$	
955.0	$O(15)$		1036.1	$S(15)$	
957.8	$O(14)$		1038.6	$S(16)$	
960.5	$O(13)$		1041.0	$S(17)$	
963.6	$O(12)$		1043.5	$S(18)$	
966.6	$O(11)$		1045.8	$S(19)$	
969.5	$O(10)$		1048.4	$S(20)$	
971.3	—		1050.7	$S(21)$	
2745.3†		$2\nu_6(Q_{max})$	1052.8	$S(22)$	

*Excited by Hg4347.
†Excited by Hg4047.

these branches are weak because of the low value of I_A/I_B. Also, the regions in which the more intense P and R lines should fall are occupied by two bands which are interpreted as $2\nu_6$ and $2\nu_2$ excited by Hg4047. The former band with a maximum at 978.0 cm.$^{-1}$ from Hg4358 must correspond to a line measured by Bhagavantam at 975 cm.$^{-1}$ and assigned by him as ν_3 of the isotopic molecule $H_3C^{12}—C^{13}H_3$. However, the intensity of the 978.0 cm.$^{-1}$ line decreases by a large factor when the sodium nitrite filter is used, indicating that the line is excited by Hg4047 and has therefore a frequency shift of 2745.3 cm.$^{-1}$. A weaker maximum at 982.1 cm.$^{-1}$ was proved by the same method to be excited by Hg4358 and undoubtedly can be assigned to ν_3 of $H_3C^{12}—C^{13}H_3$; a simple calculation based on a diatomic approximation gives the value 979 cm.$^{-1}$ for this frequency.

Various methods of reduction of the experimental data can be used to obtain molecular constants from the O and S lines of a totally symmetric Raman band. The lines can be represented as a single series in powers of J up to the fourth, and the constants ν_0, B_0, D_J, B_1, and $D_{J'}$ obtained by a regression solution. Also, combination sum and difference relations involving the O and S lines may be set up and used for the solution. However, when the constants B_0 and D_J of the ground vibrational state are known fairly accurately, the best approach is probably to accept these values and to solve only for the constants of the upper vibrational state. Thus, for the *observed* frequency shift $S(J)$ and the *calculated* ground state rotational term $F_0(J)$, the following relation holds,

$$S(J)+F_0(J) = \nu_0+B_1(J+2)(J+3)-D_{J'}(J+2)^2(J+3)^2,$$

where ν_0 is the origin of the band, and the terms involving D_{JK} and D_K are neglected. When the appropriate relation is written down for each line of the band, the best values of ν_0, B_1, and $D_{J'}$ follow from a regression solution. This procedure gave the values $\nu_0 = 994.75$, $B_1 = 0.6551$, and $D_{J'} = 17.6 \times 10^{-7}$ cm.$^{-1}$ for the ν_3 band.

The 1350–1600 cm.$^{-1}$ Region

With a gas pressure of 3 atm. and a 48 hr. exposure using the sodium nitrite filter extensive structure was observed in the 1350–1600 cm.$^{-1}$ region (Fig. 2(*a*)). A careful examination showed that most of the lines could be ascribed

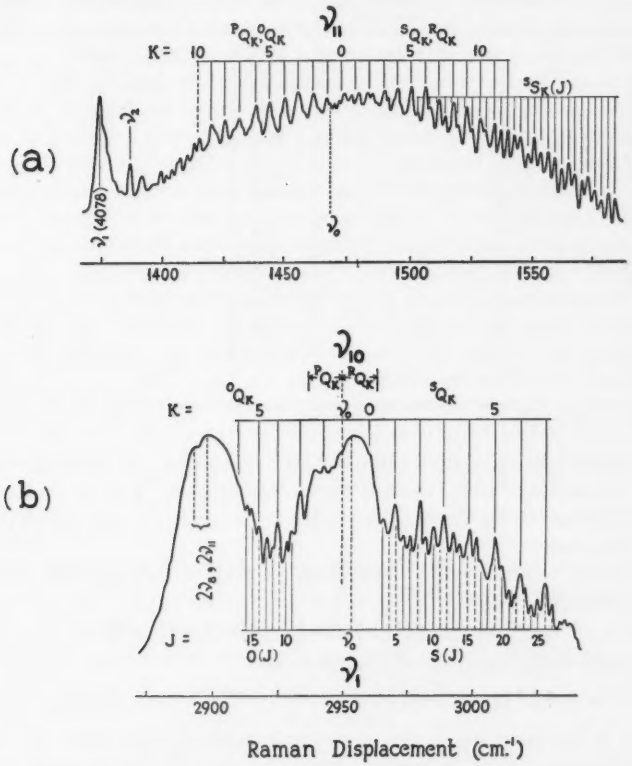

FIG. 2. Microphotometer traces of Raman spectra of ethane. (*a*) The 1350–1600 cm.$^{-1}$ region showing the ν_{11} band and the Q branch of ν_2. (*b*) The 2850–3050 cm.$^{-1}$ region showing the ν_{10} and ν_1 bands.

to the doubly degenerate ν_{11} band, previously observed as a broad unresolved band by Griffiths (5). A weak sharp line at 1388.4 cm.$^{-1}$, excited by Hg4358, does not appear to belong to the ν_{11} band and was assigned to the Q branch of the totally symmetric ν_2 vibration (Figs. 1(*b*) and 2(*a*)). This frequency has

not been previously observed and has usually been given the value 1375 cm.$^{-1}$ as calculated from the infrared $\nu_2+\nu_6$ band.

The strongest lines in the ν_{11} band form a single series with an average spacing of 5.70 cm.$^{-1}$ and must be interpreted as a series of Q branches (Table IV). Since the analysis of the ν_{10} band, which will be discussed below, proves

TABLE IV

RAMAN FREQUENCIES OF C_2H_6 IN THE 1350–1600 CM.$^{-1}$ REGION

$\Delta\nu$ (cm.$^{-1}$)	Assignment		$\Delta\nu$ (cm.$^{-1}$)	Assignment	
	ν_{11} Band	Other features		ν_{11} Band	Other features
2954.0*		$\nu_1(Q_{max})$	1525.6	$S_K(J)$	
1388.4		$\nu_2(Q_{max})$	1529.0	$^{R,S}Q_{10}$	
1425.8	$^{P,O}Q_8$		1531.1	$S_K(J)$	
1438.0	$^{P,O}Q_6$		1534.8	$^{R,S}Q_{11}$	
1443.7	$^{P,O}Q_5$		1537.1	$S_K(J)$	
1449.8	$^{P,O}Q_4$		1540.1	"	
1455.2	$^{P,O}Q_3$		1542.8	"	
1461.3	$^{P,O}Q_2$		1545.5	"	
1489.7	$^{R,S}Q_3$		1548.5	"	
1495.1	$^{R,S}Q_4$		1551.1	"	
1500.7	$^{R,S}Q_5$		1553.9	"	
1503.2	$S_K(J)$		1556.6	"	
1506.4	$^{R,S}Q_6$		1559.3	"	
1508.2	$S_K(J)$		1562.0	"	
1512.1	$^{R,S}Q_7$		1565.2	"	
1514.8	$S_K(J)$		1567.6	"	
1517.8	$^{R,S}Q_8$		1571.0	"	
1519.9	$S_K(J)$		1573.2	"	
1523.2	$^{R,S}Q_9$				

*Excited by Hg4078.

that the point group of the molecule is $\mathbf{D}_{3d}$, it must be assumed that the single series observed in the ν_{11} band is due to the accidental superposition of the $^{O,S}Q_K$ and the $^{P,R}Q_K$ lines. The following considerations show that this is indeed the case.

The Raman shifts for the $^{O,S}Q_K$ branches ($\Delta K = \pm 2$) can be represented by the formula

$$\nu_0^{sub} = \nu_0+4[A(1+\zeta)-B]\pm 4[A(1+\tfrac{1}{2}\zeta)-B]K,$$

and for the $^{P,R}Q_K$ branches ($\Delta K = \pm 1$) by

$$\nu_0^{sub} = \nu_0+[A(1-2\zeta)-B]\pm 2[A(1-\zeta)-B]K, \qquad K = 0, 1, 2, \ldots,$$

where ζ is the constant of the vibrational angular momentum and the rotational constants, A and B, are assumed to be the same for the upper and lower vibrational states. Assuming Smith's values, $A = A_0 = 2.589$ and $B = B_0 = 0.6626$ cm.$^{-1}$, the observed spacing of the lines gives $\zeta = -0.374$ for an $^{O,S}Q_K$ series and $\zeta = -0.370$ for a $^{P,R}Q_K$ series.

When these values of ζ are used, the above frequency formulae become

$$\nu_0^{sub} = \nu_0+3.83\pm 5.77K$$

for the $^{O,S}Q_K$ series, and

$$\nu_0^{sub} = \nu_0+3.84\pm 5.82K$$

for the ${}^{P,R}Q_K$ series. Thus, the lines in the two series have not only the same spacing but, within the limit of the error of observation, the lines with the same K value in the two branches are actually superimposed.

Each of the Q_K branches is accompanied by rotational wings with $O_K(J)$, $P_K(J)$, $R_K(J)$, and $S_K(J)$ branches ($\Delta J = \pm 1, \pm 2$). These branches would be expected to overlap to form an almost continuous background under the stronger Q lines. The irregularly spaced weak lines at the low frequency side of the band and near the band origin (Fig. 2(*a*)) are examples of the complex structure resulting from the overlapping rotational wings in regions where the Q lines are weak. However, on the high frequency side of the band a well-developed series of lines with an average spacing of 2.78 cm.$^{-1}$ is observed. This spacing is almost equal to $4B_0 = 2.65$ cm.$^{-1}$, so that the lines must be interpreted as an $S_K(J)$ series. It is apparent that the single series observed must actually consist of several overlapping series with different K values, which are more or less in step with one another; this situation can exist since the S line spacing is 2.78 cm.$^{-1}$, i.e. practically one-half of the Q branch spacing, 5.70 cm.$^{-1}$. This fortuitous emergence of an extended S series permits a more complete analysis of the band than would otherwise be possible.

The first step in the detailed analysis was to determine the K numbering of the Q_K lines, and thus the approximate position of the band origin. For this purpose the relative intensities of the Q_K lines, assuming coincidence of the ${}^{O,S}Q_K$ and ${}^{P,R}Q_K$ lines, were calculated using the matrix elements of Placzek and Teller (11) and statistical weights modified by nuclear spin. The calculated intensities showed, particularly in the ${}^{O}Q_K$ branch, a pattern of intensity alternation (strong, weak, weak, . . .) which was also evident in the observed spectrum. With this criterion two possible positions for the band origin came into consideration. One position was near the center of gravity of the total intensity of the band; the other allotted a greater intensity to the high frequency side of the band, in accordance with the theoretical distribution. The latter position was therefore chosen as the band origin, giving the K numbering as in Fig. 2(*a*) and Table IV.

The frequencies of the ${}^{O,S}Q_K$ lines follow the relation

$$\nu_0^{\text{sub}} = \nu_0 + 4[A_1(1+\zeta) - B_1] \pm 4[A_1(1+\tfrac{1}{2}\zeta) - B_1]K + [(A_1 - B_1) - (A_0 - B_0)]K^2,$$

when the centrifugal stretching is neglected. A regression analysis of 15 observed frequencies gave the following values for the coefficients:

$$\nu_0 + 4[A_1(1+\zeta) - B_1] = 1472.5,$$
$$A_1(1+\tfrac{1}{2}\zeta) - B_1 = 1.431,$$
$$(A_1 - B_1) - (A_0 - B_0) = -0.00782.$$

A further relationship between the constants, $2A_1\zeta = -(A_1 - B_1)$, is obtained from the fact that the line spacing must correspond to the spacings for both the ${}^{O,S}Q_K$ and the ${}^{P,R}Q_K$ series. The equations can then be solved to give $\nu_0 = 1468.7$, $A_1 - B_1 = 1.9076$, $A_1\zeta = -0.9538$, and $A_0 - B_0 = 1.9154$ cm.$^{-1}$.

The separation, $\delta\nu$, of a given $S_K(J)$ line from the corresponding Q_K line is given by

$$\delta\nu = B_1(J+2)(J+3) - B_0J(J+1)$$
$$= 6B_1 + (5B_1 - B_0)J + (B_1 - B_0)J^2.$$

Since the $S_K(J)$ lines are composite, J values cannot be assigned to the individual lines; however, when the frequencies are plotted against arbitrary but correctly ordered integers a straight line is obtained showing that the quadratic term in the above equation is negligible for the observed lines. The slope of the graph, calculated by a least squares analysis of 14 $S_K(J)$ frequencies unblended with Q_K lines, gave $5B_1-B_0 = 2.780$ cm.$^{-1}$. Using $B_0 = 0.6626$ cm.$^{-1}$, the following constants were calculated: $B_1 = 0.689$, $A_0 = 2.578$, $A_1 = 2.597$ cm.$^{-1}$, and $\zeta = -0.366$.

The determination of the origin of the ν_{11} band permits an evaluation of the torsional frequency, ν_4. The infrared spectrum shows a perpendicular band with $\nu_0 = 1747.1$ cm.$^{-1}$ and $\zeta = -0.354$, according to the analysis of Smith (13). This band has been assigned to the combination tone, $\nu_{11}+\nu_4$, and the equality of the ζ value with that of the ν_{11} Raman band shows that the assignment is correct. The ν_4 fundamental frequency, apart from a small anharmonic correction, is therefore 278.4 cm.$^{-1}$. It is interesting to note that the value, 275 cm.$^{-1}$, obtained from specific heat data by Kistiakowsky, Lacher, and Stitt (9) is very close to that obtained here. As pointed out in the Introduction, the overtone $2\nu_4$ should be active in Raman scattering; however, spectrograms in the 400–700 cm.$^{-1}$ region did not show this band even with prolonged expcsure times.

If a potential function of the form $V = \frac{1}{2}V_0(1-\cos 3\chi)$ is assumed for the torsional oscillation, the mechanical frequency ω_τ is given by $\omega_\tau = 6\sqrt{V_0 A}$, where A is the rotational constant of the whole molecule about the axis of symmetry. With $\omega_\tau = 278.4$ cm.$^{-1}$ and $A = 2.578$ cm.$^{-1}$, the calculated value of the height, V_0, of the potential hill is 835 cm.$^{-1}$.

The 2850–3050 cm.$^{-1}$ Region

An exposure time of two hours was sufficient to record the strong doublet with maxima at 2898.0 and 2953.7 cm.$^{-1}$, which has been observed at lower dispersion (10, 5). There is no doubt that this doublet is the totally symmetric C—H stretching vibration, ν_1, with its intensity divided by a Fermi degeneracy. In the high dispersion spectrograms the component at 2953.7 cm.$^{-1}$ appears to have the greater intensity and is therefore essentially ν_1. The second component has two maxima, the strong one at 2898.0 and a weaker one at 2892.7 cm.$^{-1}$; they are assigned here to $2\nu_8$ and $2\nu_{11}$, in Fermi degeneracy with each other and with ν_1. These components are broad and without any resolved structure; the intensity of the stronger component is degraded towards higher frequencies, that is, towards the stronger component of the doublet. This characteristic is fairly general for the weaker member of a Fermi doublet in high dispersion spectrograms. Since the component at 2953.7 cm.$^{-1}$ retains the characteristics expected for a totally symmetric band, it is assigned to ν_1, although this assignment is the opposite of that usually given (6).

The Q branch of ν_1 consists of four lines (Fig. 1(a)) with intensities decreasing from the lowest to the highest frequency approximately as 64 : 16 : 4 : 1. A polarization experiment (14) showed that all four lines are highly polarized and are therefore undoubtedly components of the same Q branch. The reason for the splitting of the Q branch is believed to be an anharmonic interaction

of the ν_1 vibration with the ν_4 torsional vibration. Since the frequency of the latter vibration is low (278.4 cm.$^{-1}$) there are appreciable populations in the lower excited states at room temperature. A calculation of the Boltzmann function shows that the intensities of the transitions ν_1, $\nu_1+\nu_4-\nu_4$, $\nu_1+2\nu_4-2\nu_4$, and $\nu_1+3\nu_4-3\nu_4$ are approximately in the proportion observed for the four components. If the anharmonic term in the vibrational energy formula is represented by $x_{14}(v_1+\frac{1}{2})(v_4+\frac{1}{2})$, the spacing of the components is x_{14}; the average spacing observed gives $x_{14} = 2.3$ cm.$^{-1}$.

In long exposures the 2850–3050 cm.$^{-1}$ region of Raman shifts excited by Hg4047 showed a very complex structure of lines (Fig. 2(*b*)). The frequencies given in Table V were measured from microphotometer traces of a spectrogram

TABLE V

RAMAN FREQUENCIES OF C_2H_6 IN THE 2850–3050 CM.$^{-1}$ REGION

$\Delta\nu$ (cm.$^{-1}$)	Assignment		
	ν_{10} Band	ν_1 Band	Other features
2892.7 2898.0			$2\nu_{11}(Q_{max})$ $2\nu_8(Q_{max})$
2915.4	$^0Q_5$		
2918.0		$O(14)$	
2921.0		$O(13)$	
2923.2		$O(12)$	
2924.8	$^0Q_4$		
2928.6		$O(10)$	
2930.9		$O(9)$	
2933.7	$^0Q_3$		
2939.3		$O(6)$	
2942.6	$^0Q_2$		
2945.8			?
2948.9			?
2951.9			?
2953.7		$\nu_1(Q_{max})$	
2956.2		$\nu_1+\nu_4-\nu_4(Q_{max})$	
2958.7		$\nu_1+2\nu_4-2\nu_4(Q_{max})$	
2960.7		$\nu_1+3\nu_4-3\nu_4(Q_{max})$	
2963.1		$S(3)$?	
2965.9		$S(4)$?	
2970.0	$^8Q_1$		
2973.0		$S(6)$	
2975.6		$S(7)$	
2979.1	$^8Q_2$		
2981.6		$S(9)$	
2984.6		$S(10)$	
2988.6	$^8Q_3$		
2992.0		$S(13)$	
2994.6		$S(14)$	
2998.2	$^8Q_4$		
3001.1		$S(16)$?	
3002.9		$S(17)$	
3005.4		$S(18)$?	
3008.3	$^8Q_5$		
3011.0		$S(20)$	
3013.8		$S(21)$	
3018.2	$^8Q_6$		
3022.1		$S(24)$	
3025.0		$S(25)$	
3027.4	$^8Q_7$		
3030.2		$S(27)$	

obtained with a medium-grained Cramer photographic plate with 38 hr. exposure and a gas pressure of 3 atm. Most of the lines can be arranged in two extended overlapping series with average line spacings of 9.3 and 2.7 cm.$^{-1}$. The weaker series with the spacing 2.7 cm.$^{-1}$ is clearly the O and S branches of the ν_1 band, and the stronger series with the larger spacing must be a Q_K series of the doubly degenerate ν_{10} band. With the assignment of J values as in Table V, a least squares analysis of the O and S lines of the ν_1 band, assuming $B_0 = 0.6626$ and $D_J = 6\times10^{-7}$ cm.$^{-1}$, gave the constants $\nu_0 = 2953.8$, $B_1 = 0.6619$, and $D_{J'} = 2.7\times10^{-7}$ cm.$^{-1}$.

If the series of Q lines of the ν_{10} band is interpreted as ${}^{P,R}Q_K$ lines, the observed spacing, 9.3 cm.$^{-1}$, leads to a value of ζ which is less than -1; since this is an impossible solution the lines must belong to the ${}^{O,S}Q_K$ branch. From this fact alone it can be deduced, using Table I in the Introduction, that the point group of the ethane molecule is $\mathbf{D}_{3d}$. The spacing, 9.3 cm.$^{-1}$, for the ${}^{O,S}Q_K$ lines leads to a ζ value of 0.31, and to a calculated spacing of 2.4 cm.$^{-1}$ for the ${}^{P,R}Q_K$ lines. Although no series of lines with this spacing is observed, the unresolved feature on the low frequency side of the Q branch of ν_1 can undoubtedly be interpreted as the ${}^{P,R}Q_K$ series; it has approximately the required extent and can be reasonably explained in no other way. Since the resolution obtainable with the spectrograph used is ample to resolve sharp lines 2.4 cm.$^{-1}$ apart, it must be assumed the Q_K lines are broadened by the inexact superposition of the various $J \rightarrow J$ transitions which constitute the lines. The presence of both ${}^{P,R}Q_K$ and ${}^{O,S}Q_K$ series confirms the assignment of the molecule to the $\mathbf{D}_{3d}$ point group. The structure of the ν_{10} Raman band thus constitutes the best criterion which has yet been obtained for the configuration of the ethane molecule.

The assignment of K values to the ${}^{O,S}Q_K$ lines, given in Table V, is based on a comparison of the calculated pattern of intensities with that observed. A regression analysis of the frequencies, carried out as for the ν_{11} band, gave the following relations:

$$\nu_0+4[A_1(1+\zeta)-B_1] = 2960.7,$$
$$A_1(1+\tfrac{1}{2}\zeta)-B_1 = 2.307,$$
$$(A_1-B_1)-(A_0-B_0) = 0.01194.$$

The six unknowns in these equations can be reduced to four by using the values $B_0 = 0.6626$ and $A_0 = 2.578$ cm.$^{-1}$. The solution then gives $\nu_0 = 2950.0$, $A_1-B_1 = 2.127$, and $A_1\zeta = 0.760$ cm.$^{-1}$. With the approximation $A_1 = A_0$, the ζ value is 0.256.

Summary of the Raman Results

The more important molecular constants derived from the analysis of the Raman bands of ethane are summarized in Table VI.

TABLE VI

MOLECULAR CONSTANTS DERIVED FROM THE RAMAN BANDS OF C_2H_6

Vibration	ν_0 (cm.$^{-1}$)	B_1 (cm.$^{-1}$)*	A_0 (cm.$^{-1}$)	A_1 (cm.$^{-1}$)	ζ
ν_1	2953.8	0.6619			
ν_2	1388.4(Q_{max})	—			
ν_3	994.8	0.6551			
ν_4	(278.4)†	—			
ν_{10}	2950.0	—	—	—	0.256
ν_{11}	1468.7	0.689	2.578	2.597	−0.366
ν_{12}	—	—	—	—	(0.238)‡

*The infrared value (13), $B_0 = 0.6626$ cm.$^{-1}$, was assumed.
†Calculated from $\nu_{11}+\nu_4$ and ν_{11}.
‡Calculated from the sum rule, $\zeta_{10}+\zeta_{11}+\zeta_{12} = B_0/2A_0$.

The Infrared Combination Bands

The frequencies and ζ values obtained from the Raman spectra allow some headway to be made in the assignment of the infrared combination bands observed by Smith (13). The bands at 1747.1 and 2218.0 cm.$^{-1}$ are undoubtedly $\nu_{11}+\nu_4$ and $\nu_9+\nu_2$. The following assignments can be made, provided a discrepancy of 0.05–0.10 in the calculated and observed ζ values of the combination band is tolerated: $\nu_9+\nu_{11} = 2277.1$, $\nu_{10}+\nu_4 = 3257.8$, $\nu_6+\nu_{10} = 4334.1$, $\nu_8+\nu_{10} = 4416.7$, and $\nu_7+\nu_{10} = 5950.7$ cm.$^{-1}$. No plausible assignment can be obtained for the bands at 2021.6, 2800, 2860, and 4178.9 cm.$^{-1}$.

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DIURNAL VARIATIONS IN THE NUMBER OF SHOWER METEORS DETECTED BY THE FORWARD-SCATTERING OF RADIO WAVES

PART II. EXPERIMENT[1]

By P. A. Forsyth, C. O. Hines, and E. L. Vogan

ABSTRACT

The theory developed in Part I is applied to derive the expected diurnal variations of the meteor signal rate for four showers as observed by means of a particular forward-scatter transmission path (Cedar Rapids – Ottawa). These results are then compared with the experimental signal rates. The good agreement obtained indicates that the approximations inherent in the theory are sufficiently accurate for practical purposes. The results also indicate that very few meteors, if any, are observed under conditions which do not satisfy the requirements for specular reflection.

INTRODUCTION

In Part I of this paper (4) an approximate theory was developed to account for the large diurnal variations which often occur in the rate at which meteors of a given shower are detected by the forward-scattering of radio waves from the ionized trails. Here, in Part II, the theory is applied to a specific transmission path at present in use (3), and the diurnal variations predicted by the theory are compared with those actually observed.

APPLICATION OF THE THEORY

The theory of Part I—in particular, formula [21] for F_0*—is applied directly in this section to the transmission path used in the experimental measurements (Cedar Rapids – Ottawa). The resultant contour chart, for the 'observability' of a shower as a function of the position of its radiant, differs from that given previously for two essential reasons: the transmitter–receiver separation is now 1350 km., rather than 1000 km. as had been assumed for the purpose of illustration, and the antenna pattern of the transmitter differs markedly from the one previously assumed. The first of these modifications is simple and direct, and its effects are relatively small; the second is more involved, and merits further discussion.

The transmitting antenna at Cedar Rapids (1) is highly directional, with an angular width to half power in the main lobe of approximately 5° or 6°. It is beamed at an elevation of 7° towards Stirling, Va., some 32° to the south of a direct line to Ottawa. It is reasonable to expect some low level of power outside the main lobe, and, in particular, at least two principal side lobes (down 10 db., say, from the maximum). A likely pattern of transmitted power has been assumed, for computational purposes, and incorporated in Fig. 1. This figure gives a contour chart for the illumination factor G (= the geometric mean of transmitting and receiving antenna gains) appropriate to a standard meteor

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level of 100 km. above the earth's surface. The assumed principal transmitting antenna lobes are indicated, but they are distorted in this figure by the effect of the receiver antenna pattern. The latter pattern is roughly that of a five-element Yagi, beamed toward the 100 km. level over the mid-point of the Cedar Rapids to Ottawa path, as used in the experimental work.

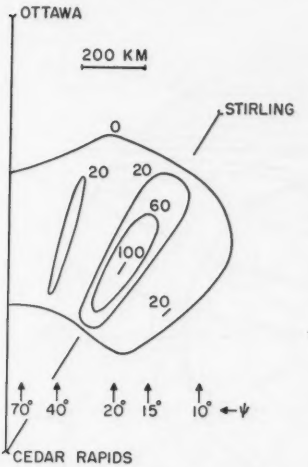

FIG. 1. Illumination pattern assumed for the Cedar Rapids – Ottawa transmission path.

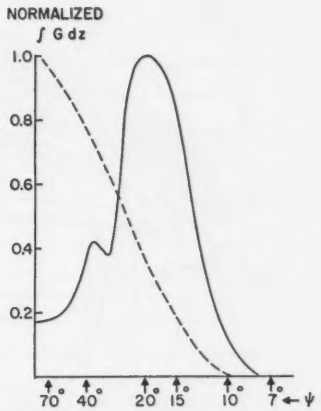

FIG. 2. Normalized illumination integral derived from Fig. 1 (solid curve), and as derived for illustration in Part I (broken curve).

The theory involves the integral of G along lines parallel to the transmitter–receiver axis TR. The appropriate line depends on an angular coordinate ψ, defined in Part I, and is indicated in Fig. 1 for several ψ's. (ψ is effectively a longitude coordinate on the celestial sphere, measured in a system having TR as axis and the $\psi = 0$ meridian in the vertical plane through TR.) The normalized integral is shown in Fig. 2 (solid curve) together with the corresponding integral for the simpler antenna system assumed in the earlier work (broken curve). The difference is striking, and the resultant changes in the 'observability' contours are appreciable; the general trend of these contours remains the same, however.

In addition to the essential modifications, a new system of coordinates has been employed in displaying the present contour chart: a celestial system, with 'declination' and 'hour angle after lower transit' as the explicit independent variables. (Such a change is possible, and advisable, once a specific transmission path is under consideration.) The latitude and longitude of Cedar Rapids (taken as 42.0° N., 92.0° W.) and of the Ottawa site (45.4° N., 75.9° W.) determine the colatitude of the mid-point (46.3°) and the azimuth of Ottawa from the mid-point (74°). These two quantities are required for the coordinate trans-

formation as outlined in Part I. The longitude of the mid-point (83.9° W.) corresponds to a difference of 36 min. between local time at the mid-point and standard time at Ottawa. This is taken into account in the following comparison between observation and theory.

The transformed, normalized contour chart of shower observability is displayed in Fig. 3. The north celestial pole lies at the center, with circles of

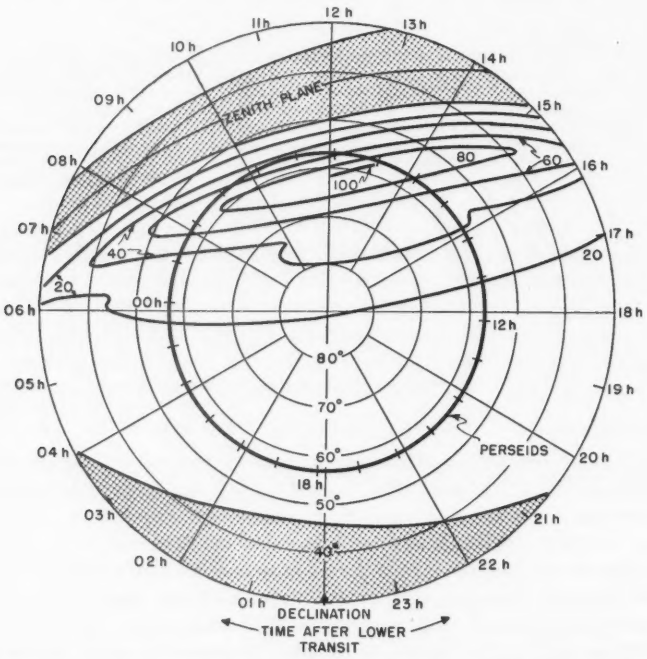

FIG. 3. Observability contour chart for the Cedar Rapids – Ottawa transmission path.

constant declination about it and lines of constant hour angle (measured after lower transit as viewed from the mid-point) radiating from it. The cross-hatched areas correspond to zero observability, and no contours are drawn in the blank area at the top left because of extreme uncertainty concerning the transmitting antenna pattern to the north of the Cedar Rapids to Ottawa direction.

The path followed by the radiant of the Perseids is shown for illustration, assuming a declination of 57° and a right ascension of 47°; the hours marked on it apply on August 12, near the height of the shower. In application, corresponding paths were drawn for the other showers observed, and graphs of the observability as a function of time were drawn up for each case. These were integrated over periods of one hour (or, for the Perseids, two hours), corre-

sponding to the periods over which the number of detected meteor trails was summed. The results are displayed by the various histograms in Fig. 4, where the vertical scale is determined quite arbitrarily by the normalized observabil-

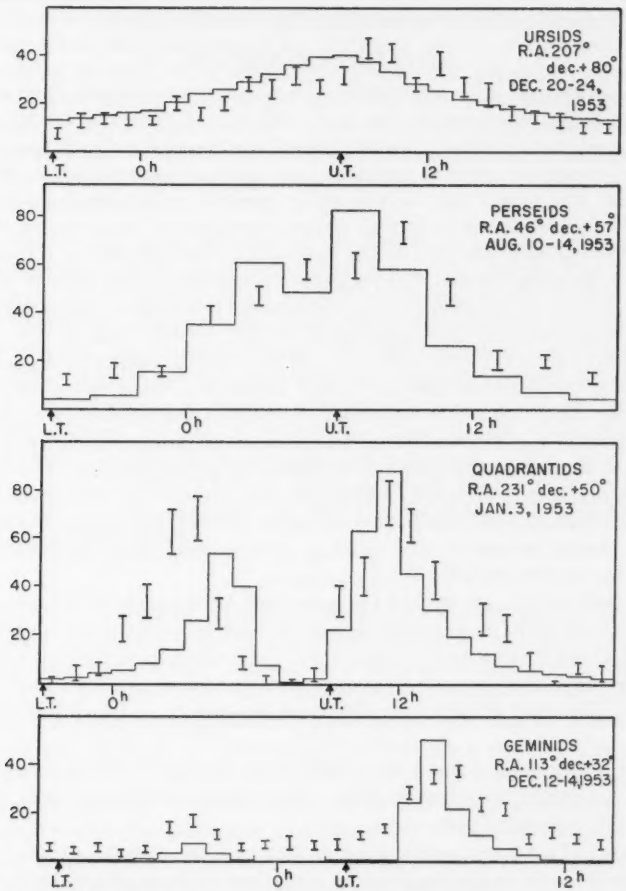

FIG. 4. Relative meteor signal rate as observed (vertical bars) and as predicted theoretically (histogram) for four meteor showers detected on the Cedar Rapids – Ottawa transmission path. The vertical scales are arbitrary, and bear no observational relationship with one another. The points marked L.T. and U.T. correspond to the times of lower and upper transit, respectively, as seen from the mid-point, whereas the hour markers indicate eastern standard time.

ity values employed in Fig. 3. The horizontal time scale is marked in eastern standard time, beginning, in each case, with the hour which includes lower transit of the radiant as seen from the mid-point.

Characteristically for this path, a radiant with a small polar distance leads

to a single theoretical maximum near the time of upper transit. As the polar distance increases, the one maximum splits into two; these two separate, and eventually a null develops between them near the time of upper transit. A third maximum could grow out of the null, but cannot be predicted accurately because of uncertainties in the transmitting antenna pattern.

EXPERIMENTAL RESULTS

The experimental data reported in this paper were obtained from records similar to those presented in Fig. 1 of Reference 3. The number of signals which exceeded an arbitrary amplitude level was counted for each hour during a shower, except at times of circuit failure (about five per cent of the total time), and the values for corresponding periods on successive days were averaged. The relative standard deviation was derived from the total count associated with each average, on the assumption that the meteor signals were randomly occurring events. The results were normalized for each of the four showers in turn, to provide a ready comparison with the corresponding theoretical histogram; they are represented by the vertical bars in Fig. 4. The total count associated with each vertical bar can be estimated by squaring the ratio of the height of the bar to half its length. About 400 meteors were counted for the Quadrantids and about three times this number for each of the other showers. In each case, the pertinent dates are indicated in the figure.

Sporadic meteors contribute to the experimental counts, but to an extent which is unknown and which varies from one shower to another (since the arbitrary counting level was varied according to circumstances). No attempt has been made to remove the sporadic meteor rate from the data, nor to account for it theoretically.

From the figure it is seen that the agreement between the experimental and theoretical values of meteor signal rate is most promising. The showers are arranged in order of increasing distance of the radiant from the north celestial pole. The development and subsequent separation of the two maxima are apparent. The four showers are discussed separately in the following paragraphs.

Ursids.—The radiant has a very small polar distance (10°) and as a result, for this particular transmission path, the shower gives rise to only a small variation in the signal rate.

Perseids.—The larger polar distance (33°) of the Perseid shower radiant causes an increase in the variation of its apparent strength on the path. The total variation in signal rate is large and even though the values may be influenced by sporadic meteors, it is not difficult to infer the presence of the shower from the experimental data. This is the shower for which the radiant path is plotted in Fig. 3.

Quadrantids.—The separation of the two predicted peaks with increasing polar distance of the radiant is complete in this shower (polar distance 40°). The corresponding two peaks are identified easily in the experimental results. The null in the experimental values at 7–8 hr. indicates that the reference level for the signal count was sufficiently high to eliminate effectively the

influence of sporadic meteors. Although the signal rates were derived from only one day's observations (because of the short duration of the shower), the results seem to be statistically significant. The earlier theoretical peak is displaced in time relative to the corresponding experimental peak. This is probably due to an error in the assumed illumination function of the Cedar Rapids antenna, since the position of this particular peak is very sensitive to the illumination function. It is interesting to note that the upper transit of this shower occurs shortly after 9 hr., at which time both the theoretical and experimental signal rates are low in spite of the very large number of shower meteors entering the atmosphere. This emphasizes the point made in Part I that a large part of the observed diurnal variation is introduced by the method of detection employed.

Geminids.—The polar distance of the shower radiant is sufficiently great (58°) that the radiant spends some time below the horizon. The null in the theoretical values between 12 hr. and 18 hr. corresponds to radiant positions below the horizon. The experimental values during this interval must be due to the sporadic meteor background. The other period of low signal rate between 22 hr. and 5 hr. corresponds to overhead radiant positions. No theoretical estimates are given for the signal rates between 23 hr. and 2 hr. During this period the radiant is south of the vertical plane through Cedar Rapids and Ottawa, and it is difficult to estimate the magnitude of the signal rate, although it certainly should be low. The magnitude of the theoretical peak at 20 hr. is also uncertain because the theory is not likely to be reliable at such low values of observability.

DISCUSSION

The agreement between theory and experiment is encouraging. The numerous small discrepancies may be attributed reasonably to inaccuracies in the assumed antenna radiation patterns, as well as to normal fluctuations in the meteor rate. It would seem that the cylindrical approximation upon which the theory is based (4) is sufficiently accurate for practical purposes.

The theoretical treatment followed from Eshleman's expression for forward-scattering of radio waves from meteor trails (2). This theory assumes that the condition for specular reflection (that the incident and reflected rays make equal angles with the trail axis) is satisfied for all observable meteors. The variation of reflected power (which in turn affects the observability) with aspect of the meteor trail is given, in part, by the factor

$$\sin^2 \alpha / (1 - \cos^2 \beta \sin^2 \phi),$$

where the numerator is a polarization factor, β is the angle between the trail axis and the plane containing transmitter, receiver, and reflection point, and ϕ is one-half the forward-scattering angle. The form of a theoretical signal rate graph is critically dependent upon the assumption of specular reflection. The factors involving β and ϕ in the foregoing expression affect the result strongly only when the observability is low, at which time the theory is unreliable for other reasons. It would seem then that the experimental results support the

assumption of specular reflection, but do not constitute an adequate test of the Eshleman expression. It may, however, be inferred from the results that the angular dependence can not be much stronger than that suggested by Eshleman.

The very sharp null in the experimental data for the Quadrantids, obtained at a time when the shower radiant was high in the sky, indicates clearly that no significant fraction of the signals was received by means of non-specular reflection. This result may be contrasted with the back-scatter experience of McKinley (5), who found an appreciable number of long-duration echoes, associated with non-specular scattering, during a similar period of unfavorable radiant position. It will be of interest to determine the accuracy of the predicted shower rates for measurements made at lower frequencies. Such measurements, which are now in progress (3), should indicate the relative importance of non-specular reflection with decreasing frequency.

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A NOTE ON THE SPIN AND PARITY OF 2.69 DAY Au^{198} *

By L. G. Elliott, M. A. Preston,† and J. L. Wolfson

In an investigation of the disintegration of Au^{198} including a study of the shape of the 1371 kev. β-ray transition to the ground state of Hg^{198}, the authors (2, 6) concluded that the parity of the 2.69 day state of Au^{198} was odd and that its spin was 1, 2, or 3. Arguments were then advanced to show that a spin value of either 1 or 2 was inconsistent with the experimental data. In particular, using formulae given by Greuling (3), it was found that the characteristic α-shape required by an assignment of 2− to the 2.69 day state of Au^{198} did not adequately represent the measured shape of the 1371 kev. β-ray spectrum. It was further found that an assignment of 3− was consistent with the spectrum shape.

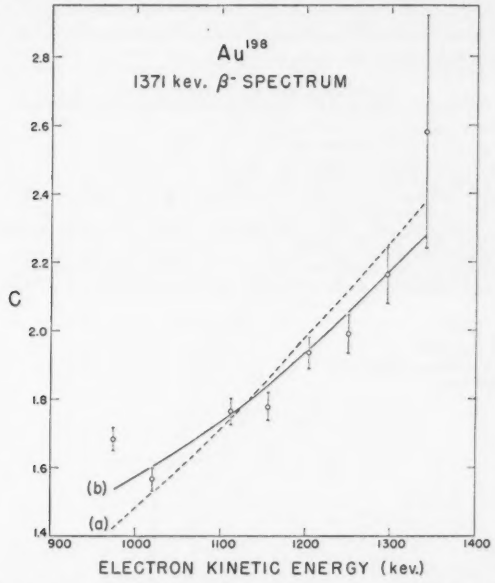

FIG. 1. The shape of the high energy Au^{198} β-spectrum, above 975 kev. The experimental data are plotted in the form of a shape factor C where $C = (N/\eta^2 F)(E_0 - E)^{-2}$. The end point of the spectrum, E_0, is taken to be the sum of the energies of the 959 kev. β-transition and 412 kev. γ-ray transition. The dashed curve (*a*) gives the theoretical shape factor for a $\Delta I = 2$ (yes) transition as calculated from the equations of Greuling (3), while the solid curve (*b*) gives the shape factor calculated from the tables of Rose *et al.* (5). The curves have been normalized to the experimental points by the method of least squares.

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A measured value of 2 for the spin of 2.69 day Au^{198} has recently been reported (4). This has prompted a reanalysis of the data obtained in the study of the 1371 kev. spectrum. In Fig. 1 the data obtained from two separate runs using different sources have been combined and are plotted in the form of an experimentally derived shape factor C (2), where $C = (N/\eta^2 F)(E_0 - E)^{-2}$. The dashed curve (*a*) gives the shape factor C_{1T} as calculated from equations 11, 12, and 14 of Greuling (3), assuming an assignment of 2− for Au^{198}. The solid curve (*b*) gives the shape factor C_{1T} as calculated from the more recent accurate tables of Rose *et al.* (5), which were not available to the authors at the time of the original analysis. The experimental data are quite well represented by the curve (*b*) and it appears that the original disagreement between the experimental shape and theoretical α-shape was due to the approximate nature of the shape factor as given by Greuling's equation 14. On the basis of our reanalysis we conclude that a spin and parity assignment of 2− (or 3−) for the 2.69 day Au^{198} is consistent with the measured spectra shapes.

The $\log f_0 t$ of the 1371 kev. β-transition is 11.7. Using the curves of Davidson (1) a value of 11.3 is obtained for $\log f_1 t$. It is interesting to note that this value is rather higher than the values normally obtained for $\log f_1 t$ of $\Delta I = 2$ (yes) transitions which generally lie between 8 and 9.

The authors wish to thank Dr. G. Lee-Whiting for discussions concerning this question.

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LETTERS TO THE EDITOR

Under this heading brief reports of important discoveries in physics may be published. These reports should not exceed 600 words and, for any issue, should be submitted not later than six weeks previous to the first day of the month of issue. No proof will be sent to the authors.

The Dependence of Meteoric Forward-scattering on Antenna Patterns and Orientations*

Radio transmission between widely separated stations, at frequencies well above the ionospheric MUFs, has received much attention recently. Specular scattering from ionized meteor trails appears to be the operative process in the case of many strong transient signals. This process has also been suggested as the one responsible for the more continuous background signal (2, 3, 5, 6), although the alternative suggestion of non-specular scattering from random blobs of ionospheric ionization (1) has received equal support. Each of these suggestions has been associated with a particular set of observational data, although its possible application to the other set of data has not been ignored in subsequent discussion.

After much debate, it has become apparent that both interpretations may be correct, but that each must be applied to a restricted class of observations. It seems the controversy can be resolved by reference to the antenna patterns employed experimentally. The highly directive characteristic of "ionospheric scattering" (1) implies that by far the most useful radio energy is that beamed towards the scattering region over the mid-point of the transmitter-receiver axis, *TR*. On the other hand, it has been shown that the most favorable regions for "meteoric scattering" lie to the sides of the *TR* axis (2). Accordingly, highly directive antennae beamed over the *TR* axis would favor the observation of ionospheric scattering, whereas broad-beamed antennae, or antennae beamed to one side of the axis, would favor the observation of meteoric scattering. These antenna characteristics are exactly those to be found in the different experimental arrangements which led to the respective interpretations.

To illustrate the importance of off-axis propagation in meteoric scattering, two sets of theoretical curves are presented here. They apply to meteoric scattering observations over a 1000 km. path, when the transmitting and receiving antennae are beamed at an angle α to one side of the *TR* axis, and at an elevation δ such that the two maxima intersect at a height of 100 km. in the mid-plane right-bisecting *TR*. The beam width between half power points is taken to be δ in elevation and ω in azimuth, with maximum antenna gain equal to $1/\omega\delta$ in order to keep the total sensitivity constant. (See Fig. 1.) The curves illustrate the effect of (*a*) broadening the antenna beam ($\alpha = 0$, ω varying; dotted curves), (*b*) swinging a narrow beam off to the side ($\omega = 8°$, α varying; broken curves), and (*c*) swinging and broadening the beam, maintaining its edge along *TR*, as in a beam split by interferometric methods ($\alpha = \omega$, both varying; solid curves). The curves in Fig. 2 give the numbers of signals to be observed above a given level,

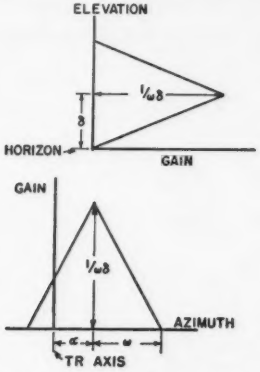

FIG. 1. Schematic diagram of assumed antenna gain.

**The work was performed under D.R.B. projects PCC No. D48-95-11-01 and PCC No. D48-28-35-05.*

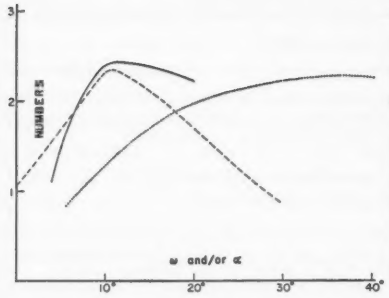

FIG. 2. Numbers of meteors producing received signals above a given level (arbitrary scale).

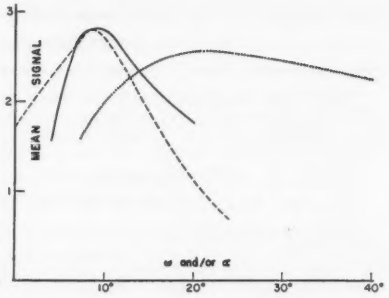

FIG 3. Mean signal level produced by meteoric forward-scattering (arbitrary scale).

..... $\alpha = 0$, ω varying; – – – – $\omega = 8°$, α varying; ——— $\alpha = \omega$, both varying.

per unit time (arbitrary scale). The curves were obtained by combining earlier theory (4) with an assumed isotropic incidence pattern of sporadic meteors. The varying durations of meteor signals, as predicted theoretically (2), have been incorporated in deriving the curves in Fig. 3, and these curves therefore indicate the relative general level of the mean background signal, obtained under the different circumstances.

The curves illustrate clearly the advantage of off-axis transmission in the case of meteoric scattering. They lend strong support to the belief that each type of scattering may indeed be operative; the dominant one being determined by the antenna pattern (at any given frequency). In addition, they may prove of value in the design of antennae to be used specifically for the study of meteoric scattering.

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